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(54) HIGH TENSILE STRENGTH COLD ROLLED STEEL SHEET EXCELLENT IN HOT DIPPING SUITABILITY AND GALVANNEALED STEEL SHEET USING THE SAME

(57)Abstract:

PURPOSE: To produce a steel sheet, as a high tensile strength steel sheet for automotive use, etc., particularly having a tensile strength exceeding 40kgf/mm2, excellent in hot dipping suitability, and satisfying other required characteristics, such as workability and secondary working brittleness resistance.

CONSTITUTION: This steel sheet is a high tensile strength cold rolled steel sheet having a composition consisting of, by mass, 0.0005-0.0050% C, 0.10-1.20% Si, 0.50-3.00% Mn, 0.015-0.100% Ti, 0.003-0.010 Nb, $\leq 0.005\%$ B, $\leq 0.100\%$ Al, 0.040-0.130% P, $\leq 0.010\%$ S, \leq 0.0050% N, one or ≥2 kinds among the oxides of rare earth elements selected from the group consisting of La, Ce, Pr, Nd, Gd, and Y by 0.0004-0.18%, in total, expressed in terms of rare earth elements, and the balance Fe with inevitable impurities. It is preferable to regulate the grain size of the oxides of the rare earth elements to ≤100nm.

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CLAIMS

[Claim(s)]

[Claim 1] C:0.0005 - 0.0050mass% and Si:0.10 - 1.20mass%, Mn: 0.50 - 3.00mass% and Ti:0.015 - 0.100 mass%, Nb: 0.003 - 0.010 mass%, less than [B:0.005 mass%], aluminum: Less than [0.100 mass%], P:0.040 - 0.130 mass%, Less than [S:0.010 mass%] and less than [N:0.0050mass%] are included. And they are the cold rolled high tensile strength steel sheets which contained a total of 0.0004 to 0.18 mass% by rare-earth-elements conversion, and were excellent in the hot-dipping nature which the remainder becomes from Fe and an unescapable impurity in one sort of the oxide of rare earth elements chosen from from among La, Ce, Pr, Nd, Gd, and Y, or two sorts or more. [Claim 2] Cold rolled high tensile strength steel sheets which were excellent in the hot-dipping nature to which particle size of the oxide of rare earth elements is characterized by being below 100 nm in claim 1.

[Claim 3] The alloying hot-dip zinc-coated carbon steel sheet which comes to form an alloying hot-dip-zincing coat on a steel plate front face according to claim 1 or 2.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[Industrial Application] The application to which comparatively severe processing is performed mainly as an object for automobiles etc. is presented with this invention, and it relates to suitable cold rolled high tensile strength steel sheets and the hot-dip zinc-coated carbon steel sheet using it. [0002]

[Description of the Prior Art] Many steel plates which were made to contain Ti, Nb, etc. which are a carbon nitride formation component in order to use super-low carbon steel as the base and to improve workability and aging nature as cold rolled sheet steel which has the outstanding moldability conventionally, as JP,56-139654,A etc. has a publication, were made to contain strengthening components, such as P, further in the range which does not injure workability, and attained high intensity-ization are proposed. however, the reinforcement of these steel plates -- tensile strength (T. S.) -- at most -- 40kgf/mm2 it is -- there was a limitation in high intensity-ization. Then, as another problem originating in containing Si and Mn so much in this steel plate, although there is a proposal about the cold rolled sheet steel which made JP,59-193221, A contain Si further that-izing of this steel plate should be carried out [high intensity] further, i.e., a steel plate for the automobiles which a front planar problem (for example, degradation of degradation of chemical conversion nature and hot-dipping nature) cannot mainly avoid easily, and are made into the purpose, use cannot be borne at all. Moreover, also about the steel plate of the component system which made P contain so much as a strengthening component, there was a trouble of secondary elaboration-proof brittleness deteriorating. [0003] How to return, after oxidizing a steel plate compulsorily by the high oxidation part draft in advance of heat treatment, in order to improve degradation of the above-mentioned plating nature (JP,55-154554,A etc.), Or although the methods (JP,58-104163,A etc.) of performing pre plating etc. are proposed before performing hot dipping By these approaches, since stable plating's necessarily not being guaranteed depending on the component in steel and plating conditions since control of the scaling object at the time of heat treatment is not enough, and an excessive process were added, there was a trouble that cost went up.

[0004]

[Problem(s) to be Solved by the Invention] as the high-tensile-steel plate used for automobiles in this invention -- especially -- tensile strength -- 40kgf/mm2 what is exceeded -- it is -- in addition -- and that in which hot-dipping nature excelled is set as the main development purpose. such a high-tensile-steel plate -- high tension, hot-dipping nature, and workability (mechanical property) -- it is an indispensable condition to fulfill further all properties demanded in the purpose for spending, such as secondary elaboration-proof brittleness. Although there are some which conflict mutually in these properties, a better property is required without the property of another side being inferior as compared with the conventional steel plate. the automobile according [the purpose of using such a steel plate] to thinning etc. -- lightweight -- since it is-izing, even if it compares secondary elaboration-proof brittleness [win] with other properties, it is required by deteriorating, when raising reinforcement that a severe condition

should be satisfied extremely. Furthermore, it is required that these demand characteristics should be realized from a viewpoint of the cost reduction of an automobile, without adding an excessive process. [0005] Then, this invention sets it as that purpose to propose cold rolled high tensile strength steel sheets excellent in the plating nature and deep drawability which satisfy the above-mentioned conditions by all means. This steel plate can also make it natural to make it an alloying hot-dipping steel plate by giving hot dip zincing and carrying out heating alloying. [0006]

[Means for Solving the Problem] The main point of this invention is the purpose which controls the scaling object at the time of heat treatment, in order to improve ** hot-dipping nature. In order to make the oxide of rare earth elements, such as La, Ce, Pr, Nd, Gd, or Y, contain and to raise ** workability Super-low carbon steel is made into a fundamental component, suitable amount addition of Si, Mn, and the P is carried out, a still higher r value is obtained by compound addition of Ti and Nb, and B is made to contain for reservation of secondary elaboration-proof [**] brittleness.

[0007] This invention Namely, C:0.0005 - 0.0050mass% Si:(only hereafter shown by %)0.10-1.20%, Mn:0.50-3.00%, Ti: 0.015 - 0.100 %, Nb:0.003 - 0.010 %, B: Below 0.005 %, below aluminum:0.100 %, P:0.040 - 0.130 %, Below S:0.010 % and N:0.0050% or less are included. And La, A total of 0.0004 - 0.18% is contained for one sort of the oxide of rare earth elements chosen from from among Ce, Pr, Nd, Gd, and Y, or two sorts or more by rare-earth-elements conversion, and they are cold rolled high tensile strength steel sheets (the 1st invention) excellent in the hot-dipping nature which the remainder becomes from Fe and an unescapable impurity.

[0008] Moreover, this invention is cold rolled high tensile strength steel sheets (the 2nd invention) excellent in the hot-dipping nature to which particle size of the oxide of rare earth elements is characterized by being below 100 nm in the 1st invention.

[0009] By being able to use the steel plate of the 1st invention and the 2nd invention as an alloying hot-dip zinc-coated carbon steel sheet by forming an alloying hot-dip-zincing coat on a steel plate front face, and controlling the burning unevenness at the time of alloying processing, and avoiding the alloying rate delay by P, since this alloying hot-dip zinc-coated carbon steel sheet is excellent in plating adhesion, consequently excellent in corrosion resistance, it is desirable.

[0010]

[Function] Artificers found out the following operations, as a result of repeating various examination about the component which a steel plate is made to contain, in order to improve the alloying property in the case of considering as an alloying hot-dip zinc-coated carbon steel sheet to the deep drawability of a steel plate, and a hot-dipping nature pan. First, by making the oxide of rare earth elements, such as La 2O3, CeO2 and Pr 2O3, Nd 2O3, Gd 2O3, and Y2O3 grade, contain in a total of 0.0004 - 0.18% of range by rare earth conversion the front face of Si system oxide (SiO2, Fe2SiO4, Mn2SiO4, MnSiO3 grade) which the amount of oxidation of a scaling layer decreases, and checks hot-dipping nature after annealing -- concentration is controlled.

[0011] Moreover, P which delays an alloying rate remarkably is adsorbed on the front face of the above-mentioned rare-earth-elements system oxide, and concentration near the grain boundary is controlled. [0012] Furthermore, it was thought that it was the cause of the burning unevenness at the time of alloying, and it became clear that dispersion in the internal oxidation layer of the steel plate surface section which is had the breakaway (exfoliation) nature of the surface scale at the time of hot-rolling and correlation. Furthermore, relation between the breakaway nature of a surface scale and the amount of isolation-among steel S was, and it became clear that breakaway of a surface scale became remarkable, so that there were many amounts of isolation-among steel S. This is presumed because burning unevenness generating at the time of alloying can be prevented by controlling breakaway of a surface scale by the front face of a rare-earth-elements system oxide being adsorbed in S, and stabilizing, and controlling dispersion in the internal oxidation layer of the steel plate surface section.

[0013] Moreover, about tensile strength, workability, etc. of a steel plate, the improvement which also

[0013] Moreover, about tensile strength, workability, etc. of a steel plate, the improvement which also combined properties, such as secondary elaboration-proof brittleness, by rationalizing the combination of Si, Mn, and P and making B contain after carrying out the proper amount residual of the dissolution C

was realized, and it resulted that the very good quality of the material was acquired as compared with the conventional steel type in a header and this invention.

[0014] Hereafter, the reason limited about the component presentation range by this invention is explained.

Although it is desirable to make it decrease from a viewpoint of improvement in elongation and an r value as for C:0.0005 - 0.0050%C content, when fewer than 0.0005%, it brings about degradation of secondary elaboration-proof brittleness, or the fall of a weld zone (heat affected zone) on the strength and is not desirable. Moreover, decreasing rather than 0.0005% also industrially does not balance in cost. On the other hand, when C content exceeds 0.0050%, since a remarkable quality-of-the-material (especially ductility) improvement effect is not acquired even if it makes Ti of the equivalent, and Nb contain, and there are a steel-manufacture process, a hot-rolling process, and a possibility of producing un-arranging in other production processes further, it is not desirable. Therefore, C content was limited to 0.0005 - 0.0050% of range.

[0015] Si: 0.10% was made into the minimum as a limit where sufficient strengthening effectiveness is first acquired as an Si content 0.10 to 1.20%. Although what is necessary is just to adjust Si content according to the level of target tensile strength fundamentally, when it is made to contain exceeding 1.20%, in order that a hot-rolling motherboard may harden notably, in addition to cold-rolling nature deteriorating, degradation of chemical conversion nature etc. also becomes remarkable. It is in the inclination which further various internal defects also increase and is not desirable. Therefore, the upper limit of Si content was made into 1.20%.

[0016] Mn: When Mn is made to contain independently 0.50 to 3.00%, the mechanical property after cold-rolled annealing, especially an r value are degraded, but when it uses together with other components and is made to contain in 0.50 - 3.00% of range, a strong rise can be aimed at, without being accompanied by remarkable degradation of the quality of the material. Unless it fills Mn content here to 0.50%, sufficient strengthening cannot be obtained, but if it exceeds 3.00% on the other hand, as a result of a steel plate's hardening remarkably, big difficulty is caused at a cold-rolled process. Therefore, Mn content was limited to 0.50 - 3.00% of range.

[0017] Ti: 0.015 - 0.100 %Ti is an indispensable component in order to aim at improvement in an r value. Although the improvement effect of an r value becomes remarkable by content of 0.015 % of Ti, even if it makes it contain exceeding 0.100 %, in addition to being saturated, it becomes remarkable deteriorating [of surface treatment nature] the effectiveness. Moreover, when Ti is made to contain exceeding 0.100 %, they are an r value and El. It became clear that a fall is also remarkable. Therefore, the minimum of Ti content was limited to 0.015 %, and the upper limit was limited to 0.100 %, respectively.

[0018] Nb: An r value higher than the case of independent content of Ti can be obtained by making 0.003% or more of 0.003-0.010 %Nb(s) contain. Moreover, it is advantageous in order for there to be effectiveness which controls the unusual grain growth at the time of annealing and to obtain homogeneity and a detailed steel plate organization by content of Nb. Moreover, it is effective also to an improvement of the shape of front planarity. However, Nb When it is made to contain exceeding 0.010%, the inclination for secondary elaboration-proof brittleness, ductility, and an r value to deteriorate is shown. Moreover, the effectiveness is not acquired unless Nb content fulfills 0.003 %. Therefore, it limited to Nb content and 0.003 - 0.010 %.

[0019] B: 0.005% or less B is this effectiveness although it is a component effective in the improvement of secondary elaboration-proof brittleness. It is saturated with 0.005% and there is a possibility of causing the fall of workability on the contrary depending on annealing conditions. Moreover, a hotrolling motherboard is also hardened notably. Therefore, B content made 0.005% the upper limit. In addition, although what is necessary is just to contain an initial complement according to extent of an improvement of secondary elaboration-proof brittleness which should not be limited and should be desired especially about a minimum, it is desirable to contain 0.0015% or more.

[0020] aluminum: If 0.100% or less aluminum is effective in defecation of steel and removal of inclusion is enough, even if it is aluminum non-contained steel substantially, degradation of a property will be

presumed to be what is not. However, when it was made to contain exceeding 0.100%, since it led to front planar degradation, the upper limit was limited to 0.100 %.

[0021] P: While reinforcement increases by making 0.040 - 0.130 %P contain, workability (mainly r value) improves notably further. It is remarkable at this effectiveness and 0.040% or more of content. On the other hand, it is P. When it is made to contain exceeding 0.130%, as a result of the segregation at the time of coagulation becoming very firm, in addition to the increment in strong being saturated, degradation of workability is caused, still larger degradation also about secondary elaboration-proof brittleness is caused, and use is not borne on parenchyma. Therefore, upper limit It could be 0.130%. [0022] S: Below 0.010 % S is a component to reduce as much as possible also from a viewpoint of alloying unevenness, as mentioned above. It contributes to the sludges in steel decreasing in number, workability improving, and the effective amount of Ti which fixes C improving by reducing the amount of S. Such effectiveness is S content. It is obtained by considering as 0.010% or less. In addition, since the rare-earth-elements system oxide made to contain by this invention is effective in adsorbing S, it is contributed to reduction of the amount of S.

[0023] By reducing the amount of N N:0.0050% or less, improvement in the quality of the material (especially ductility, an r value) is expectable. However, in addition to the effectiveness may be mostly satisfied with decreasing to 0.0050% or less of effectiveness being acquired, since the further reduction caused the increment in cost, it made the upper limit 0.0050%.

[0024] one sort of the oxide of rare earth elements chosen from from among La, Ce, Pr, Nd, Gd, and Y, or two sorts or more -- rare-earth-elements conversion -- a total of 0.0004 -- the oxide of -0.18mass% rare earth elements -- the front face of said Si system oxide -- concentration -- it is a component effective in raising the plating nature of a steel plate by decreasing a layer and controlling generation of an oxide. Moreover, there are also an operation which reduces the amount of S in steel, and an operation which avoids the alloying delay by P. As an oxide of the rare earth elements which have such operation effectiveness, although La 2O3, CeO2 and Pr 2O3, Nd 2O3, Gd 2O3, and Y2O3 can be mentioned as an example of representation, the oxide of the rare earth elements of this invention is not limited to this example of representation, and the amounts of oxygen to combine may differ. There is a problem from which the addition effectiveness which carried out expected when one sort of the oxide of rare earth elements chosen from from among La, Ce, Pr, Nd(s), Gd(s), and Y like these or two sorts or more were not filled with rare-earth-elements conversion to a total of 0.0004% is not acquired, and if it is made to contain exceeding 0.18% on the other hand, un-arranging [that distribution into that cost goes up and steel becomes difficult] will arise. Therefore, it carried out to making it contain in 0.0004 - 0.18% of range.

[0025] Moreover, as for the particle size of the oxide of rare earth elements chosen from from among these La, Ce, Pr, Nd(s), Gd(s), and Y, it is more desirable that it is below 100 nm. in order that the adsorption capacity of S on the front face of an oxide and P may decrease rapidly in exceeding 100 nm while this effect of the invention becomes still clearer, when particle size is below 100 nm -- a front face -- concentration -- it is for the alloying unevenness control by scale breakaway prevention and alloying delay depressant action to decrease in the control list of a layer.

[0026] In addition, if one sort of La, Ce, Pr, Nd, Gd, and Y or two sorts or more are added, the sulfide of rare earth elements, the nitride, etc. may be generating in addition to the oxide of rare earth elements, but in this invention, as long as it contains even the oxide of La, Ce, Pr, Nd, Gd, and Y by the specified quantity, the sulfide of these rare earth elements, the nitride, etc. may be contained.

[0027] The cold rolled sheet steel of this invention can be fundamentally obtained by performing the well-known manufacture approach. That is, whenever [slab stoving temperature] is made into 1150-1300 degrees C, and it is finish rolling temperature. The hot rolling made into 800-1000 degrees C is performed, and the cooling rate after hot-rolling is rolled round as 30 degrees C/s or more. Winding temperature It considers as 580-680 **. Cold rolling is performed after acid washing. Cold-rolled rolling reduction is made into 65% or more. Annealing is performed after that. Annealing conditions 800-900 ** and a soaking time are 20-200s. The cooling rate after annealing to carry out and 400 degree C carry out in 20 degrees C/s or more. In addition, there are an approach of producing by carrying out

neutralization precipitate and adding in molten steel, the approach of carrying out deposit control of the rare earth elements dissolved in steel in the annealing process of a steel plate, etc., distributing the hydration oxide of rare earth elements in a water solution, in order to make particle size of the oxide of rare earth elements below into 100 nm.

[0028]

[Example] The steel which becomes the various component presentations shown in Table 1 was ingoted, the cold rolled sheet steel of board thickness 0.7 mm was manufactured on the conditions shown below, and the mechanical property and hot-dipping nature, and an alloying property were investigated. The underline given to the component etc. shows the outside of this invention range. [0029]

Table 1

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	Ţi	0.042	"	<i>""</i>	<i>"</i>	"	. "	<i>"</i>	"	"	"	"	"	"	"	"	"	"	"	0.07	ú	"	<i>"</i>	10.0	0.07	"	0.042
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[0030] <conditions> -- slab stoving temperature whenever: -- 1220 - 1280-degree-C finish rolling temperature: 850 - 880 ** cooling condition: -- after finish rolling -- less than 3 seconds -- quenching initiation and about 40 degrees C/[in a second] -- cooling rolling-up temperature:520 ** cold-rolled rolling reduction:78% annealing condition:840 **, 30-second soak, and a furnace atmosphere -- N2+5% H2 cooling condition:annealing temperature to cooling rate of 25 degrees C/second up to 350 degrees C -- cooling [0031] <Mechanical property evaluation> The tractive characteristics of the obtained cold rolled sheet steel are JIS 5. The usual examining method estimated using the number test piece for

tensile test. Moreover, about secondary elaboration-proof brittleness, it is a contraction ratio 2.0. After carrying out the flange cut of the conical cup which it kept extracting, 5kg weight was dropped to various temperature from height of 80cm, the impact load was given, and the upper limit temperature which produces a brittleness-crack estimated. If this temperature is -45 degrees C or less in general, it can be judged as satisfactory level in an anticipated-use environment.

[0032] <hot-dipping nature> - hot-dipping condition bath temperature: -- 470 ** permeation board temperature: -- aluminum content [under 470 ** bath]: -- 0.15wt% plating coating weight: -- 60 g/m2 (per one side)

Plating time amount: The image processing was performed about the appearance after 1sec and the hotdipping nature evaluation approach hot dipping, and it asked for the rate of a non-galvanized area, and evaluated in accordance with the following criteria.

5: rate 0.1 of rate of 0%4of rates of non-galvanized area:non-galvanized area 0 ** - 0.1 %3:a non-galvanized area Rate 0.3 of ** - 0.3 %2:a non-galvanized area **-0.5 %1: -- un--- rate of plating area 0.5 % ** and a plating adhesion evaluation E. I. du Pont de Nemours impact test (diameter 1/4 an inch and weight with a weight of 1kg are fallen on a steel plate from height of 50cm) estimated plating adhesion. A criterion is shown below.

O:-plating-breakaway-less **: they are those with x:plating breakaway with plating breakaway [0033] to a part. <an alloying rate and alloying unevenness evaluation> - alloying condition programming-rate: -- 20-degree-C [/] s temperature fall rate: -- 15-degree-C [/] s alloying temperature: -- 490 ** alloying time amount: -- whether the zinc eta layer remains on the front face of the alloying material processed under the evaluation approach above-mentioned conditions of 30 second and an alloying rate estimated the alloying rate.

O:-zinc-eta-layer-less x: use the evaluation approach salt bath of those with a rolling eta layer, and alloying unevenness, and it is a 10x20cm hot-dipping plate 490 ** and 30 It alloyed in the second, and the plating appearance after alloying was observed and evaluated about whether there is any alloying unevenness.

O: with no burning unevenness (homogeneity)

O: burning unevenness **** has no actual harm a little.

x: Those with burning unevenness [0034] The result obtained in this way is shown in Table 2. The example according to this invention shows the good property compared with the example of a comparison so that clearly from Table 2. Moreover, the outstanding effectiveness is acquired, especially when the particle size of a rare-earth-elements system oxide is below 100 nm so that clearly from the example of steel types 13-18.

[0035]

[Table 2]

	Y.S. (kgf/mm²)	T. S. (kgf/mm²)	E . (%)	r値	溢版性選移	幹価 ^{き外観} ・	解整性	(全部)	解描むら	備考
1	32	48	39	2	80	5	0	0	0	発明例
2	31	48	39	2	-85	5	0	0	0	"
3	30	45	38	21	-80	. 5	0	0	0	"
4	30	46	38	2	80	<u>),</u> 5	0	0	0	" .
5	30	45	35	1.9	-80	<u>.</u> 5	0	Ó	0	" ·
6	31	45	35	2	-85	· 5	0	0	0	"
7	31	48	36	2	-80	5	0	0	0	"
8	30	45	38	1.9	-80	5	0	0	0	"
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10	31	ষ্ণ	38	2	-85	5	0	0	0	٠ ,,
11	35 .	32	32	2	-80	. 4	Δ	×	×	"
12	33	35	31	i. 6	-75	. 3	×	.×	× .	比較例
13	32	46	38	1.9	-80	5	0	0	0	"
14	31	48	38	1.8	-80	5	0	0	, O .	発明例
15	30	4.1	36	1.8	-80	5	٥	0	0	"
16	31	46	. 35	1.9	-80	5	0	0	. 0	.11
17	30	45	31	1.9	-80	<u>.</u> 5	0	Ō	0	" .
18	31	46	35	l. 8	-80	ž 5	0	0	Ċ.	"
19	32	47	38	ż	70	5	0 ·	×	×	比较例
20	31 .	48	35	1.5	-70	1	Δ	×	×	".
21	42	61	25	1.3	- 70	4	Δ	×	×	i
22	33	45	35	1.5	- 70	: 4	Δ	×	×	"
23	42	G5	30	1.6	-70	; 5	0	.0	٥	"
24	33	45	35	1.4	-70	<u>;</u> 5	0	Ģ	©	" .
25	30	47	36	1.8	-70	´ 5	0	0	0	"
26	33	46	32	1.5	-80	· 2	×	×	×	発明例

[0036]

[Effect of the Invention] The cold rolled sheet steel of this invention has the hot-dipping nature and deep drawability which were excellent though it was high intensity, is useful especially in the purpose for spending of an automobile etc., and is made [making board thickness mitigate, after securing the reinforcement to need, and aiming at mitigation of a body weight, and mitigation of the fuel consumption accompanying it and raising the reinforcement of each part material more and aiming at improvement in dependability and safety, or]. Since maintenance of earth environment and improvement in passive safety are attained in this way, the effectiveness is size.

[Translation done.]